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**EVALUATION OF THE POTENTIAL FOR CO₂ EVOLUTION FROM
PLUTONIUM-BEARING OXIDE MATERIALS STABILIZED AND STORED IN
CONFORMANCE WITH DOE-STD-3013-2000**

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Summary

Recent observations of CO₂ in thermogravimetric analyses of impure plutonium oxide after stabilization but prior to packaging have raised questions about whether there is significant potential for problematic buildup of CO₂ in 3013 containers during storage. In the present report we conclude that currently available information does not indicate a risk of problematic pressurization of a 3013 storage container by CO₂.

The available evidence suggests that TGA observations of CO₂ from stabilized material are explained by incomplete destruction of some carbonate compounds in the stabilization process. However, these carbonate compounds are likely to be thermally and radiolytically stable under storage conditions and will not release significant CO₂ into the 3013 container. The limited observations of CO₂ within containers of plutonium-bearing oxide materials are not likely to have been caused by decomposition of carbonate compounds.

The principal uncertainties in these conclusions stem from the heterogeneous nature and the diversity of materials to be packaged. Our conclusions are based largely on the scientific literature on the behavior of pure compounds, and on limited observations on impure materials. Shelf-life studies and surveillance activities are essential to assure that any unanticipated effects are identified and addressed.

Introduction

Several recent observations of small amounts of gases apparently evolved from impure plutonium oxide bearing materials have raised questions about whether these gases might build up to pressures threatening the integrity of 3013 storage containers. This report specifically addresses CO₂. Other gases that have been observed, including HCl, NO_x and SO₂ will be addressed in separate reports.

Small but measurable quantities of CO₂ have been observed in the gas phase within a limited number of containers of impure plutonium oxide, though not under storage conditions fully compliant with DOE-STD-3013-2000. The observations in static systems have occurred at or near ambient temperature following exposure of the material to air or to other oxygen and carbon sources. A larger number of observations of CO₂ evolution have occurred upon heating stabilized materials under flowing inert gas during thermogravimetric analysis (TGA) of stabilized material.

The purpose of this report is to summarize the existing observations, to evaluate these results in the context of available technical information, and to discuss whether they indicate a potential for pressurization or corrosion of storage containers that has not been considered to this point. The sources of information include unpublished experimental data that has been communicated to us, as well as published studies.

Potential consequences of CO₂ evolution

Pressurization and corrosion are the main concerns for compromising the integrity of a storage container. Carbon dioxide and carbonates are not credible contributors to corrosion even in the presence of liquid water. Carbon dioxide dissolved in water forms carbonic acid, a weak acid that is not a threat to stainless steel.[Lillard 2002] Therefore, we concern ourselves with the potential impacts on storage by pressurization but not by corrosion in this report.

Of secondary concern is whether evolution of CO₂ during TGA testing of stabilization may bias TGA moisture measurements. We will discuss the impacts on moisture measurement in both TGA-FTIR and TGA-MS.

Observations of CO₂ evolution

The experimental data that have raised concerns about CO₂ can be divided into observations of small amounts of CO₂ in the gas phase above stabilized material after heating or exposure to air, and observations of higher pressures of CO₂ above unstabilized material than has been neither processed nor packaged according to DOE-STD-3013-2000. To summarize, none of the experiments on stabilized material have suggested that CO₂ is likely to be generated in measurable quantities in the gas phase under storage conditions. Even the experiments on unstabilized material with an oxidant deliberately added have not suggested sufficient CO₂ generation to approach container design pressures.

Stabilized material

Carbon dioxide has been detected by mass spectrometry and infrared absorption among the gases evolved during thermogravimetric analysis of thermally stabilized, impure plutonium oxide during stabilization testing. The mass losses coinciding with CO₂ have generally been less than 0.1 % of the sample mass, but have exceeded 0.4% on occasion.

Full FTIR data are available from TGA-FTIR analysis of four impure materials at LANL. Three to four samples of each material were analyzed. Two samples of one material and one sample of another material exceeded 0.1% mass loss coincident with CO₂ evolution, but none exceeded 0.2%. The major CO₂ evolution in these runs occurred above 800° C, consistent with the CO₂ source being thermal decomposition of inorganic carbonates. Lesser amounts of CO₂ were observed being evolved from 150 to 500° C, consistent with release of adsorbed CO₂ or with alkali bicarbonate decomposition.

Recent TGA-FTIR analysis of impure stabilized oxides at RFETS have revealed at least two batches in which CO₂ evolution coincided with mass losses of 0.4 to 0.5%.[Brugh 2003] We have examined the raw TGA and FTIR data from these two batches, one set of which is summarized in Figure 1. The total mass loss by this sample

included about 0.1% moisture, most of which occurred during the step seen about 300 s into the TGA run (~150 °C). The CO₂ evolution began at about 450 °C and was not complete when the measurement ended, though the rate of evolution was decreasing. Samples of several other RFETS batches have shown smaller amounts of CO₂ evolution during TGA-FTIR measurements.

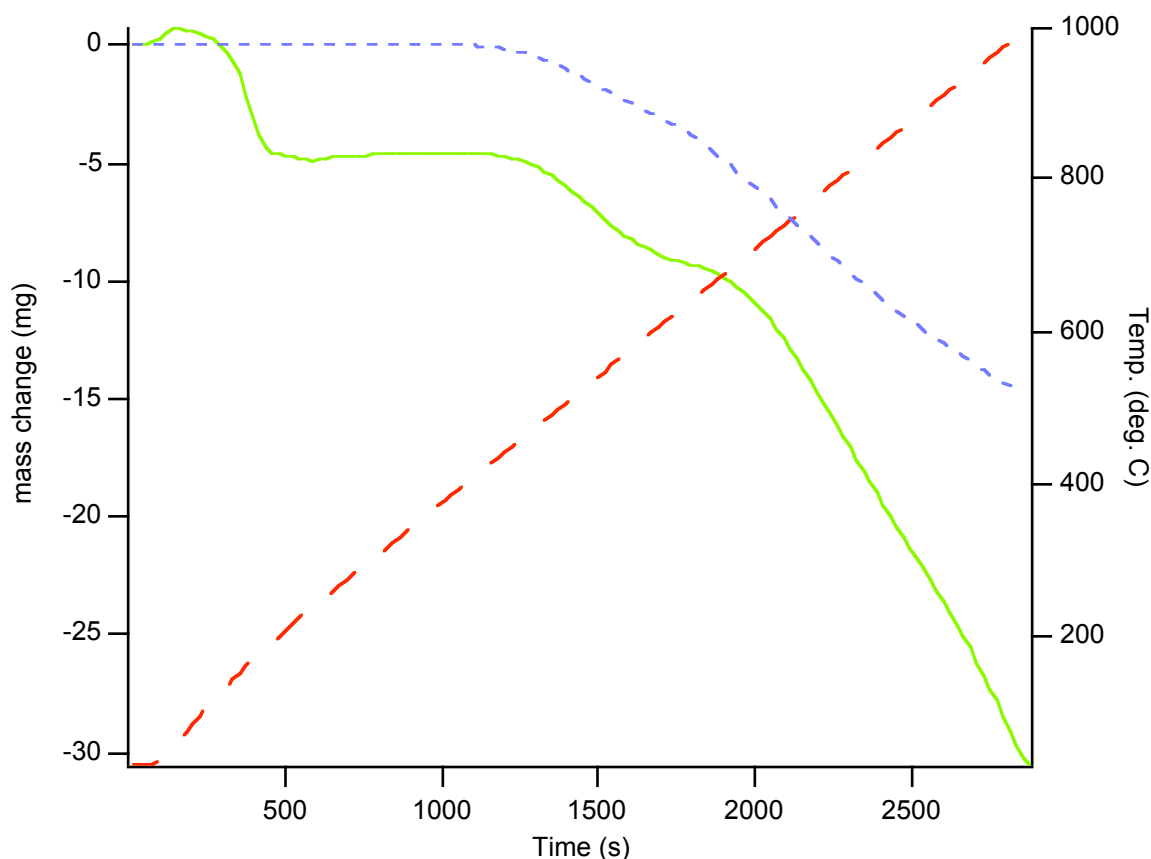


Figure 1: Partial analysis of RFETS TGA-FTIR results for a 6 gram sample showing 30 mg (0.5%) total mass loss (solid line, left axis) correlated with cumulative CO₂ IR absorbance (short dashes, left axis, arbitrary scale). The TGA temperature ramp is also shown (long dashes, right axis). The mass loss at 400 s and part of the mass loss at 1500 s are shown by the FTIR to be due to water evolution. Some of the mass loss from 2300 s through the end of the run is associated with SO₂ evolution detected by FTIR. Data source: [Brugh 2003]

Hanford has consistently observed CO₂ evolved during TGA/MS analyses of stabilized, impure plutonium oxide that was recovered from miscellaneous stored solutions by oxalate precipitation. This CO₂ is being quantified by calibrating the MS signal to a NaHCO₃ standard.[Barney 2002] None of the samples would have failed the 0.5% mass loss criterion based on CO₂ alone. Of those that failed due to total mass loss, CO₂ accounted for up to 0.15% loss. Most of the mass loss in the failed samples correlated with mass 18 MS signal and was ascribed to water.

Carbon dioxide has been detected in the gas phase over samples of both stabilized and unstabilized impure plutonium oxide materials in small, static tests conducted at LANL.

In these tests, small samples (~10 g) of plutonium bearing material were placed in sealed vessels, backfilled with either air, helium or N₂ to approximately ambient pressure, and stored for three to five years at ambient temperature. Gas chromatography and Raman spectroscopy analyses at the end of the experiments showed partial pressures of CO₂ of 2 to 4 kPa (0.3–0.6 psia) in all four valid (no evidence for container leakage) experiments that used air as the initial fill gas. Oxygen was depleted from its initial concentrations by at least the amounts required to account for the oxygen content of the observed CO₂ in these four experiments. The one experiment containing helium as the initial fill gas and known not to have leaked showed no detectable CO₂ in the gas phase. One other container initially filled with He is known to have leaked in air and showed 3 kPa (0.4 psia) CO₂ and no detectable O₂. Two samples containing N₂ as the initial fill gas showed final CO₂ partial pressures up to 2 kPa (0.3 psia) and no O₂, but it is not known whether these containers leaked. No correlation was observed between final CO₂ partial pressure and whether the material had been calcined to 950 °C or used as-received.[Veirs, Allen et al. 2002]

The first container in the Large Scale Shelf-Life Study at LANL, which is charged fairly pure plutonium dioxide stabilized to meet STD-3013 criteria, evolved CO₂ while the container was being evacuated in preparation for back-filling with helium. The temporary vacuum reduced the thermal conductivity of the contents and allowed the center-line temperature to rise to approximately 150 °C, which may have been sufficient to desorb CO₂ from oxide surfaces. The CO₂ pressure was not measured directly, though the maximum pressure achieved in the vacuum line between the pumping system and the container was about 1 kPa (0.15 psia). After two days under dynamic vacuum, the container was backfilled with helium, which reduced the centerline temperature to approximately 50 °C. The CO₂ evolution ceased with the reduction in temperature, and the CO₂ partial pressure has not exceed the detection threshold of 0.5 kPa (0.07 psia) in more than one year of observation. This material had been stored under dry air in a sealed (Conflat™ seal) container for approximately three weeks prior to the beginning of these experiments.

Unstabilized material

Savannah River, in its surveillance program, has observed CO₂ in the head-space gas within two containers of unstabilized, material stored in non-3013 packaging configurations that include plastic bags. Partial pressures of 15 kPa (2.2 psia) CO₂ and 40 kPa (5.9 psia) H₂ were measured in one container. In both cases the CO₂ and H₂ are believed to have been formed during degradation of the plastics.[Schaade 2002]

Unpublished work about five years ago at Savannah River measured gas generation from enclosed samples of 15 g of an unstabilized plutonium oxide/plutonium fluoride mixture combined with 60 g MgO containing 1 to 2 mass % carbon. The mixture was exposed to high-humidity air before sealing. Total pressures increased from roughly 100 kPa (15 psia) to roughly 160 to 300 kPa (24 - 44 psia) over the one to six week experiments. Carbon dioxide was responsible for most of the pressure increases.[Livingston 2002]

Neither of these observations are directly relevant to assessing the potential for accumulation of CO₂ above stabilized material in STD-3013 packages. They are

documented here principally because they are part of the body of available information that has raised the level of concern over CO₂.

Quantification of Potential CO₂ Storage Pressures

A conservative approach to defining maximum CO₂ pressurization risk would be to assume that all adsorbed CO₂ and carbonate compounds within a container will be converted to gas phase CO₂ during storage. The maximum temperature of the oxide material in a storage container within a 9975 shipping container during transport is calculated in STD-3013 Table A-1 to be 275 °C, and the maximum average gas temperature to be 211 °C. At those temperatures, the potential for CO₂ to raise the pressure inside the container will be the same as that of water on a molar basis, and less than half that of water on a mass basis. The acceptable level of CO₂ in the absence of other gases would be about 1.2 mass %, which is the molecular weight ratio times the 0.5 mass % standard for water. If both water and CO₂ are present, the current 0.5 mass % criteria for LOI, TGA inert, and TGA analytical techniques would be a conservative measure of CO₂ plus H₂O pressurization potential.

If CO₂ can be measured independently of H₂O prior to packaging, an acceptance criterion based on total moles of CO₂ and H₂O per kg of material could be used instead of the simple mass ratio. However, if most CO₂ detected by TGA can never become gas phase CO₂ during storage, this approach would unnecessarily increase the time and costs associated with increased analytical complexity and increased stabilization due to CO₂ related failure to meet the TGA 0.5% mass loss criterion.

An alternative approach would be to use available information to discern the forms in which CO₂ and CO₂ precursors are found in a storage container at the time of packaging, and to use this information to estimate how much of each could be converted to gas phase CO₂ during storage under the standard conditions. Relevant information may be found in published thermal decomposition and radiolysis studies of carbonates, discussed below, and in the TGA/FTIR and TGA/MS data that are being collected on stabilized materials. A small number of additional, carefully targeted experiments may be needed to verify these estimates.

Gas Generation Mechanisms

If CO₂ gas is produced during storage, it will have to originate from constituents of the 3013 container contents or the inner surface of the container. Possible generation mechanisms include radiolysis of carbonate salts, thermal decomposition of carbonate salts, thermal desorption of adsorbed CO₂, or some as yet unidentified reaction of an oxygen source with a carbon source.

Even assuming completely efficient generation mechanisms, CO₂ production would ultimately be limited by the availability of its elemental constituents, carbon and oxygen, within the container. Oxygen does not provide a useful elemental limit, of course, because there are many moles of oxygen atoms in the stored oxides. Carbon is worthy of considering more carefully. To generate 1.2 mass % CO₂ in a 5 kg batch of material, one needs $0.012 \times 5000\text{g} / 44\text{g/mole} = 1.36$ moles of carbon, which is about 16 g or 0.3 mass % of the typical contents of a storage container. Total carbon assays were performed on some of the materials represented in the MIS inventory at LANL. An

examination of these data for the few materials run in recent TGA/MS/IR qualification tests show that none exceeded 0.3 mass % carbon.

The steel of the containers might also be considered as a carbon source, but it is not a major factor. The stainless steel walls of the inner container have roughly up to 1 g of carbon, using the specified type 304 and type 316 stainless steel maximum carbon content of 0.08 %, and assuming a 1000 g container mass. Even in the highly unlikely scenario that all of the carbon in the steel could be made available for CO₂ formation, the steel would not be a major contributor to quantities of concern for pressurization. This does not rule out its contribution to the smaller amounts of CO₂ seen in small-scale experiments outlined above.

However, elemental carbon measurements are not routinely conducted prior to packaging, so one could not rely on limited carbon availability alone to rule out pressurization in production batches.

Carbonate Thermal Decomposition

Most metal ions found as impurities in stabilized material are capable of forming carbonate compounds, and most if not all of these compounds decompose upon heating between room temperature and 1000 °C, releasing CO₂. Some of the relevant information is summarized in Table 1. Note that ranges rather than specific values are given for decomposition temperatures. Decomposition temperature is not a thermodynamic parameter, but rather is most closely associated with the kinetics of the decomposition reaction. Measured ranges depend upon how the measurement is made and upon the morphology of the reactant.

Based on the overlap of these decomposition temperatures with the observed temperatures of CO₂ release detected in TGA-FTIR and TGA-MS measurements, it is reasonable to conclude that small amounts of these compounds either survive stabilization because mass and/or heat transfer rates limit overall decomposition rates. Alternatively, some carbonate compounds could form in small amounts during cooling after stabilization. DOE-STD-3013-2000 states the expectation that carbonate compounds will have decomposed completely during stabilization above 950° C for 2 hours.[DOE-STD-3013-2000, Appendix A, p. 28] A recent comprehensive review of thermal decomposition studies of ionic solids points out that kinetics for some carbonate decompositions are influenced by many experimental variables, including the morphology of the reactant, the rate that CO₂ diffuses away from the oxide product, and variations in the CO₂ or inert gas overpressure that is present.[Galwey and Brown 1999]

The influences of experimental parameters are illustrated by CaCO₃ decomposition, which has been extensively studied. Many of the effects are explained as originating from the reversibility of the reaction.[Galwey and Brown 1999] The reverse reaction between CaO(s) and CO₂(g) to form CaCO₃ has been shown to occur relatively rapidly under 1 atmosphere of CO₂ at temperatures as low as 50° C under some conditions, and to be dependent on the method in which the CaO is produced.[Maciejewski and Reller 1989] In all cases the measured rates were sufficient for the carbonation reaction to be essentially complete in a few hours at 300 °C.

Table 1: Thermal decomposition parameters of selected metal carbonate salts whose elemental constituents are known to exist in stabilized material. Values are from tabulations in [Galwey and Brown 1999], except for the uranium carbonate data which are taken from [Chernorukov, Knyazev et al. 2002].

Compound	Products	Decomposition Temperature Range (° C)	ΔH (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)
CaCO ₃	CaO, CO ₂	661-740	178	205
MgCO ₃	MgO, CO ₂	540-600	116.9	150
(Mg,Ca)CO ₃	MgO, CaO, CO ₂	577-667		208-230
NaHCO ₃	Na ₂ CO ₃ , CO ₂ , H ₂ O	110-124	71.8	109
KHCO ₃	K ₂ CO ₃ , CO ₂ , H ₂ O	121-136	79.0	93
UO ₂ CO ₃	U ₃ O ₈ , CO ₂ , O ₂	410-500		
Na ₄ UO ₂ (CO ₃) ₃	Na ₂ UO ₇ , CO ₂ , Na ₂ O (reacts with crucible)	450-530 (first stage) 800-900 (second stage)		

Significant dependence of the apparent decomposition temperature on sample bed depth and heating rate have been documented for bed depths from 0.1 to 0.5 cm (20 to 300 mg sample masses) and heating rates of 1 to 10 deg./min. in a TGA apparatus for both CaCO₃ and MgCO₃. [Sharp, Wilburn et al. 1991; Wilburn, Sharp et al. 1991; Wilburn and Sharp 1993] Decomposition temperatures were observed to vary by more than 100 °C depending on measurement conditions.

These studies are possibly relevant to understanding observations of CO₂ in TGA of stabilized materials in that they offer a plausible explanation of why some significant fraction of the original carbonate content impure materials might survive stabilization. Under stabilization conditions in which batch sizes are several kg, bed depth effects and related factors hindering CO₂ removal from the reaction zone would be much more significant than in the small scale studies summarized above. Even the CO₂ partial pressure in the air flow during stabilization (0.03 kPa) might be significant in leading to

incomplete decompositions, though we have found no data on the reverse reaction at the relevant pressure.

It is quite plausible some carbonates survive stabilization but decompose during TGA measurements due to the smaller batch size and the use of a purge gas free of CO₂. Most of the CO₂ evolution in TGA measurements has been observed at sample temperatures above 500 °C, consistent with thermal decomposition of carbonate compounds. Thus the appearance of CO₂ in TGA/FTIR and TGA/MS does not indicate CO₂ will be evolved from that stabilized material under storage conditions. Nor does the total amount of CO₂ evolved in a TGA measurement indicate how much CO₂ would be in the gas phase even at elevated temperatures in a storage container. The carbonates of the alkali and alkaline earth metals are thermodynamically favored over their decomposition products at storage temperatures. At elevated temperatures the CO₂ pressure would be limited by the consumption of CO₂ to form carbonates from oxides.

Comparison with water

For reasons presented in the following discussion, carbonate ions and adsorbed CO₂ do not present the same pressurization risks as an equal number of moles of water. There are two principal mechanisms of pressurization starting from water: hydrogen formation and water vaporization. Hydrogen and oxygen are formed when water is chemically or radiolytically decomposed. DOE-STD-3013-2000 assumes, lacking evidence to the contrary, that the H₂ is not consumed by other reactions and that it continues to be generated and builds up pressure until the available water is consumed. Evidence suggests that the O₂ can be consumed by reacting with PuO₂ to form PuO_{2+x} and will not be available for the reverse reaction with H₂ to form H₂O. Contrast this behavior of adsorbed water with that of CO₂ formed from carbonate decomposition. The reverse reactions with such oxides as CaO and MgO to re-form carbonates are known to occur at achievable storage temperatures under 100 kPa (15 psia) of CO₂. Thermodynamics strongly favor the carbonate over the oxide at storage temperatures.

A second important difference between water and CO₂ is that water can form hydrates and substantial adsorption layers on inorganic materials of high surface area when exposed to atmospheres containing easily achievable water partial pressures prior to packaging. Temperatures substantially above 100 °C that may be achieved during storage would vaporize some of this water, resulting in pressurization. In contrast, CO₂ has a much higher equilibrium vapor pressure at packaging temperatures, so it should not condense on the high surface area materials beyond perhaps a monolayer or so, and it does not undergo a dramatic increase in vapor pressure between packaging and storage temperatures. It also is not plausible that substantial pressures of CO₂ will be available in the gas to which material is exposed prior to packaging. The partial pressure of CO₂ in air is about equal to the partial pressure of water vapor in 1% relative humidity air at 25° C (0.04 kPa).

Though TGA results suggest some residual carbonates survive stabilization, as discussed above, amounts capable of being released by thermal processes at storage temperatures are quite small. Furthermore, even if radiolysis mechanisms provide an additional source of carbonate decomposition to CO₂, a conclusion not supported by the

discussion below, reviewed technical literature suggests that the reverse thermal reactions will moderate the achievable CO₂ pressures at storage temperatures.

Radiation chemistry

Non-thermal carbonate decomposition to form CO₂ must also be considered. We have performed a fairly extensive literature search on radiolysis of carbonate compounds and of CO₂, and we have not found evidence that any processes occur rapidly or extensively enough to generate significant CO₂ under storage conditions. Even if radiolytic generation of CO₂ from carbonate compounds does occur, the thermal reverse reaction remains available to consume CO₂.

The literature on the radiation effects on carbon dioxide and on solid carbonate compounds is not as extensive as for other molecular compounds due to the relative inertness of these materials to the effects of radiation. “Calcium carbonate crystals only become colored in a nuclear reactor, apparently without decomposition”, and “gaseous carbon dioxide is practically unaffected by radiation.”[Spinks and Woods] Nevertheless, radiation does have some effect, especially if water is present, which we will now discuss.

Solid State Radiolysis Effects

The principal product of carbonate radiolysis is the CO₂^{•-} radical ion trapped at low concentration within the crystal. Irradiation of anhydrous solid carbonates at room temperature forms the CO₂^{•-} radical ion, which is readily observable by electron spin resonance (ESR).[Kohno, Yamanaka et al. 1994] The G-values for α - and γ -ray production of CO₂^{•-} were obtained to be G α = 0.0041 and G γ = 0.27. The ratio of G α to G γ is known as the k-value, which is a parameter of vital importance in ESR dating.[Lyons and Brennan] The CO₂^{•-} radical ion is long lived, but does not continuously increase in concentration. The CO₂^{•-} radical ion population rapidly saturates due to recombination. When water is present to react with the CO₂^{•-} radical ion within calcium carbonate crystals at 5% and the crystals are dissolved in water after irradiation, then organic acids are observed in the water. Formic acid, CH₂O₂, is the most abundant organic acid produced by more than a factor of 10 with G = 0.018.[Albarra, Collins et al. 1994] It is not clear whether the acids are formed in the crystal prior to dissolution or are formed when the CO₂^{•-} radical ion is released during dissolution. The build-up of organic acids with time is postulated to have been important in providing organic precursors for life on the early earth when radiation fields were much stronger than they are now.

The radiolysis of carbon dioxide in the adsorbed state has been studied on zeolites and silica gel.[Sutherland, Sethi et al. 1967] The G-value for the production of CO from carbon dioxide adsorbed on molecular sieves were less than 0.5. The G-value for the production of CO on silica gel varied with outgassing conditions from 181 to 19. The reduction in CO production is attributed to the loss of surface hydroxyl groups, which promote CO formation, as the outgassing conditions become more extreme.

Reactions Involving Gases

Carbon dioxide gas is remarkably radiation resistant. This, together with advantageous heat transfer properties, has made it attractive for use as a coolant in graphite-moderated reactors.[Mozuner]. The radiolytic decomposition of CO_2 to CO and $\frac{1}{2}\text{O}_2$ has been extensively studied and is very complex. In order to account for pressure, temperature, dose rate and other effects, a model with 76 reactions and 19 species is needed.[Kummler, Leffert et al. 1977] Nevertheless, the equilibrium concentration of CO in CO_2 irradiated at 10^6 R/h is quite small, slightly greater than 250 ppm. Addition of small amounts of water to the gas phase reduces the CO concentration to less than 20 ppm.[Ikezo, Sato et al. 1981] The interaction of CO_2 with graphite in a radiation field is known to erode the graphite by the overall reaction $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$. This reaction is easily shut down by the addition of small amounts of gas-phase scavengers such as water.[Belloni, Delcourt et al. 2000] Carbon dioxide gas can also oxidize UO_2 to UO_{2+x} in a radiation field, with the CO_2 being reduced to CO.[Dominey, Morley et al. 1966]

Conclusions and Recommendations

The authors of this report conclude that the information we have examined does not indicate a significant risk of problematic pressurization of a 3013 storage container by CO_2 liberated from stabilized, impure material. We base this conclusion on published thermal decomposition and radiolysis studies of pure carbonates that may be in stored materials, and on all known available observations of gas generation by small batches of impure materials under conditions similar to storage. Net decomposition of carbonates should not occur to a significant degree by any of the mechanisms we have examined, but these mechanisms are capable of explaining the observations of CO_2 evolution during TGA analyses of stabilized material.

Of course, there is some risk associated with fact that the available information does not encompass all scenarios of stored material composition and handling history. This risk, while judged to be low, can be further mitigated by ongoing shelf-life studies in which the gas compositions above actual stabilized, stored material are monitored for long periods.

Gas-phase CO_2 has only been observed in sealed containers of stabilized material in cases where the material was exposed to air or water before sealing. These presumably serve as oxygen sources to oxidize some of the available carbon impurities to CO_2 , though the mechanisms have not been demonstrated nor have the controlling parameters been measured. Air-exposed material appears to have CO_2 generation limited by available O_2 , which was depleted from its initial pressure in those experiments. Small-scale experiments on impure materials exposed to controlled doses of oxygen have been suggested and would test our explanations of the small amounts of CO_2 that have been observed in past small-scale experiments.

The existing observations of CO_2 evolution from materials during TGA analyses can be explained by the survival of some carbonate salts through the stabilization. Literature examined for this report indicates that such carbonate survival is quite plausible due to the mass and configuration of the material during stabilization. The reversibility of some carbonate compound decompositions suggests that atmospheric CO_2 could react with material during cooling in the stabilization furnace to regenerate at least small amounts of

carbonate compounds in the stabilized product. Adsorption of small amounts of CO₂ from the air onto oxide surfaces after stabilization is also a plausible source of some of the CO₂ observed in TGA measurements.

Deliberately spiking portions of batches of impure material with pure carbonate compounds prior to stabilization and then comparing post-stabilization TGA/IR or TGA/MS of spiked and unspiked material would test the extent of carbonate decomposition during stabilization. If carbonate survival is deemed unacceptable, modification and testing of the stabilization process could be guided by the results of such tests. We emphasize, however, that from what we know now the presence of residual carbonate compounds does not present a pressurization risk.

Information search methods employed for this report

One component of the information search consisted open-source literature searches using the databases Scifinder and DOE Energy, which include Nuclear Science Abstracts, Chemical Abstracts, NTI and the DOE “grey” unclassified report literature. Keywords included relevant combinations of radiolysis, radiation damage, corrosion, carbonates, carbon dioxide and adsorption. Corresponding searches were made of current holdings in the LANL technical library.

A second component of the information search involved the collection of available DOE complex-wide empirical data on gas generation and corrosion in environments relevant to STD-3013. In particular, this included data from the DNSFB 94-1 R/D program, SRTC results related to impure actinide materials packaging and transportation and recent STD-3013-related thermogravimetric (TGA) data from Hanford, Rocky Flats and Los Alamos.

The third component of the information search involved direct interviews with individuals who are widely acknowledged subject matter experts in relevant aspects of this evaluation within the DOE community, universities and the Aldermaston Weapons Establishment (AWE).. These individuals are listed in the acknowledgement section of this report.

Sources that we examined but may not have referenced specifically in the text of this report are listed in Appendix A.

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